

# Band-structure of graphene above the vacuum level

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We study the 2D band-structure of the stand-alone graphene in the context of the bound states immersed in the 3D continuum. Depending on the symmetry of the in-plane  $\mathbf{k}$  vector, the true bound states either survive in the continuum or not. By use of a nearly exactly solvable model we demonstrate that those bound states which do not survive acquire a finite life-time, in other words they turn into resonances.

The low-lying energy bands of a stand-alone graphene are well understood. The linear dispersion of its  $\pi$  (highest occupied) and  $\pi^*$  (lowest empty) bands can be obtained analytically in the tight-binding approximation and it is known since as early as 1947 [1]. Presently, it is an easy exercise in the application of any of the existing solid-state codes to calculate the  $\pi$  as well as the lower  $\sigma$  valence bands from the first principles [2–7].

Going higher in energy, we eventually enter the continuous spectrum which corresponds to the infinite motion perpendicular to the layer. This is presented in Fig. 1, where the band-structure of graphene obtained in the repeated-geometry calculation is plotted. Inside the continuous spectrum [8], one can discern the lines entering from below the continuum. The latter have a clear interpretation: They correspond to the states of the in-plane motion but with the energy above the continuum edge [9]. If, however, one looks deeper into the problem, an important issue arises: An electron placed in a state of the in-plane motion with a sufficiently high energy has, generally speaking, a non-zero probability to escape from the layer into vacuum, which would impart this state a finite life-time, i.e., turn it into a resonance.

Since the discreet states inside the continuum, both true bound states and resonances, would play an important role in optical absorption and inverse photoemission of graphene, to mention only two experimental techniques, they deserve a close study. The latter is the subject of the present work. It must be also noted that although our discussions are centered around graphene, the significance of the problem under investigation extends beyond the latter, being pertinent to any stand-alone 2D-periodic system.

We start by considering a trivial case: Let us have a quantum well  $V_z(z)$  in  $z$  direction with the flat potential in  $xy$  plane. Then, if the well has bound states, and since the two perpendicular motions are independent, the wave-function is the product of a bound state in  $z$  direc-

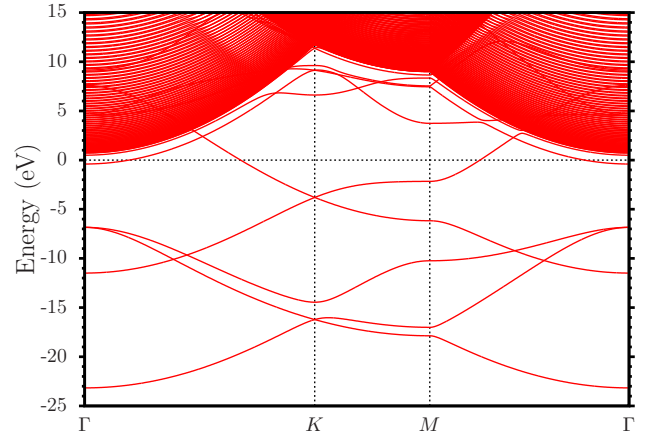


FIG. 1. (color online) The band-structure of graphene obtained in the repeated-geometry. The all-electron full-potential linearized augmented-plane wave code *Elk* [10] was used for this calculation. The separation between the periodically stacked layers is  $d = 400$  bohr.

tion and a plane wave in  $xy$  plane. As a result, there exist states which are bound within the well having an arbitrarily high energy above the vacuum level due to the motion in  $xy$  plane.

If, however, we apply a potential which is periodic in  $xy$  plane, the variables in the Schrödinger equation do not separate any more, i.e., the two perpendicular motions become coupled. To get a better insight on how this affects the high-lying energy bands of the in-plane motion, we first consider a simplified model:

*$\delta$ -function quantum well with laterally periodic potential* – We are looking for a solution of the Schrödinger equation

$$\left[ -\frac{1}{2}\Delta + V(z, \mathbf{r}_{\parallel}) \right] \psi(z, \mathbf{r}_{\parallel}) = E\psi(z, \mathbf{r}_{\parallel}) \quad (1)$$

with the model potential being a product of a periodic function in the  $xy$  plane and the  $\delta$ -function quantum well in  $z$  direction

$$V(z, \mathbf{r}_{\parallel}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}_{\parallel}} \delta(z), \quad (2)$$

where  $\mathbf{G}$  are the 2D reciprocal lattice vectors. We set  $V_0 < 0$  to ensure the existence of a state bound to the  $z = 0$  plane. The solutions of Eq. (1) with the potential (2) can be written explicitly as Bloch waves with respect to the motion in  $xy$  direction

$$\psi(z, \mathbf{r}_{\parallel}) = \sum_{\mathbf{G}} a_{\mathbf{G}} e^{i\sqrt{2E - (\mathbf{G} + \mathbf{k})^2} |z|} e^{i(\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}_{\parallel}}, \quad (3)$$

where  $\mathbf{k}$  is the in-plane wave-vector within the first Brillouin zone, and  $a_{\mathbf{G}}$  are still unknown coefficients [11]. Importantly, in Eq. (3) we have retained the exponent with one sign only, which corresponds to considering the bound and, possibly, resonant states, while omitting the scattering states with respect to the  $z$  direction motion [12]. The jump in the wave-function's  $z$ -derivative is obtained by the integration of Eq. (1) in  $z$  over the infinitesimal interval  $[0-, 0+]$

$$\psi'(0+, \mathbf{r}_{\parallel}) - \psi'(0-, \mathbf{r}_{\parallel}) = 2 \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}_{\parallel}} \psi(0, \mathbf{r}_{\parallel}), \quad (4)$$

where the prime denotes the differentiation with respect to  $z$ . Together, Eqs. (3) and (4) lead to

$$\sum_{\mathbf{G}'} V(\mathbf{G} - \mathbf{G}') a_{\mathbf{G}'} = i\sqrt{2E - (\mathbf{G} + \mathbf{k})^2} a_{\mathbf{G}}. \quad (5)$$

The crucial point is the choice of the sign of the square roots in Eqs. (3) and (5). Denoting the generic square root by  $s$ , the rule must be

$$\text{if } \text{Re } s^2 > 0 \text{ then } \text{Re } s > 0, \text{ else } \text{Im } s > 0, \quad (6)$$

which choice ensures the correct asymptotic behavior of both bound states and resonances.

The values of  $E$  which allow for non-trivial zero solutions of the homogeneous system of linear equations (5) determine the band-structure of our model system. However, in contrast to the original Eq. (1), Eqs. (5) constitute a *nonlinear eigenvalue problem* [13] with respect to  $E$ . This complication is the price paid for the separation of the bound and resonant states from the continuous spectrum.

In Figs. 2 and 3, results of the numerical solution of the non-linear eigenvalue problem (5) which give the band-structure of the stand-alone layer are presented together with the results of calculations carried out for the same system in the repeated-geometry. The symmetry of the 2D periodic potential was chosen that of a honeycomb lattice with graphene's lattice constant, and the values of the Fourier coefficients of the potential in atomic units

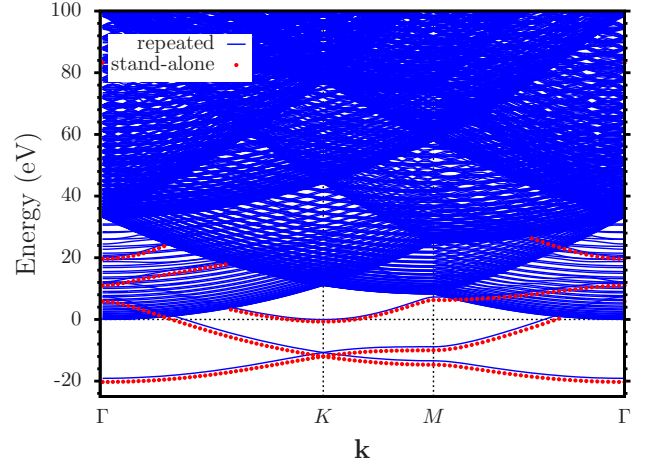


FIG. 2. (color online) Band-structure of the model system obtained with the repeated-geometry calculation (blue lines) and with solving the eigenvalue problem (5) for a stand-alone plane (red points). The calculation has been conducted along  $\Gamma - K - M - \Gamma$  line.

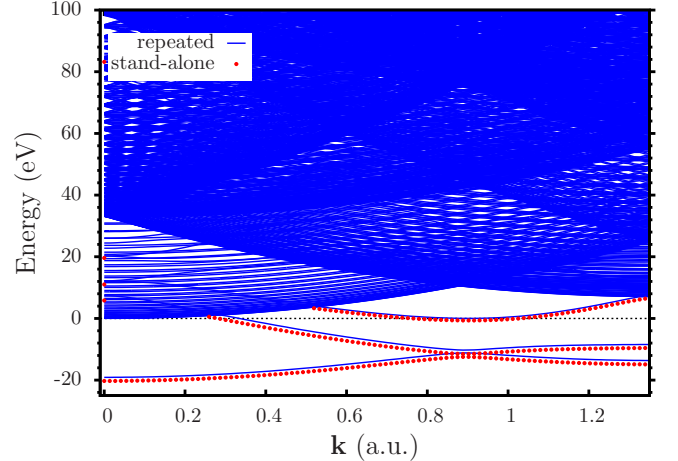


FIG. 3. (color online) The same as Fig. 2, but for the asymmetric  $\mathbf{k}$  direction along  $7\mathbf{b}_1 + 13\mathbf{b}_2$ , where  $\mathbf{b}_1$  and  $\mathbf{b}_2$  are the primitive reciprocal vectors.

were:  $V_0 = -1.093$ ,  $V_{\mathbf{G}} = 0.156$  ( $-7/10b$  and  $1/10b$ , respectively, where  $b$  is the length of the primitive vector of the reciprocal lattice) for the first  $\mathbf{G}$  star, and  $V_{\mathbf{G}} = 0$  otherwise. In Fig. 2, the wave-vector varies along the  $\Gamma - K - M - \Gamma$  lines while in Fig. 3 a completely asymmetric direction of  $\mathbf{k}$  variation is chosen. For the bands below the vacuum edge, both the repeated-geometry and the stand-alone calculations yield the identical results regardless of the symmetry of the wave-vector. In contrast, above the vacuum edge, whether or not a particular state localized near  $z = 0$  survives as a true bound state is determined by the symmetry of the corresponding  $\mathbf{k}$  point. For the totally asymmetric case of Fig. 3, there are no such states. As can be seen from Fig. 2, along the sym-

TABLE I. Eigenenergies (in eV) for the model system obtained with the reduced size of  $V(\mathbf{G} - \mathbf{G}')$  matrix permitting the fully analytical solution of the non-linear eigenvalue problem (5).

$\Gamma$	$K$	$M$
-20.3	-11.9	-13.9
5.8	-0.6	-9.5
11.0	26.0 - 0.2 i	7.7
19.6	26.8 - 0.6 i	9.8 - 0.6 i
24.3 - 1.4 i	28.5 - 0.9 i	39.4 - 0.7 i
80.1 - 0.9 i	55.9 - 0.2 i	42.1 - 0.3 i
80.9 - 0.6 i	61.6 - 0.6 i	59.6 - 0.8 i
82.4 - 0.2 i	61.6 - 0.7 i	
83.2	64.6 - 0.8 i	
116.5 - 0.2 i	127.7 - 0.6 i	
116.8 - 0.6 i	127.7 - 0.5 i	
117.3 - 1.3 i	160.8 - 0.5 i	

metric directions some of the bound state bands do survive. Moreover, an isolated high-lying bound state exists in the  $\Gamma$  point.

While the results in Figs. 2 and 3 elucidate the issue of the bound states survival above the vacuum edge, they do not answer the question what happens with those which do not survive, i.e., do the latter turn into resonances by acquiring finite life-times or they disappear at all. This is due to our numerical search for the eigenvalues of the nonlinear eigenproblem (5) having been restricted to the real axis of  $E$ , since no decisive numerical procedure exists to either find all complex-valued roots of this problem or to prove their absence. To shed the light on the latter issue, we have also been solving the eigenvalue problem (5) analytically for the sizes of the  $V(\mathbf{G} - \mathbf{G}')$  matrix admitting such a solution within a reasonable time. Using the *Mathematica* symbolic algebra software, we have been analytically evaluating the determinant  $\Delta(E)$  of the system (5), consecutively eliminating the square roots from the equation  $\Delta(E) = 0$ , which permitted its reduction to the polynomial equation. All roots of the polynomial equation (including the complex ones) have then been found with no loss of any of them guaranteed. Since spurious zeros have been largely introduced when reducing the equation to the polynomial, the roots were finally sorted retaining only those which satisfied the original equation  $\Delta(E) = 0$ . This has been done for  $\Gamma$ ,  $K$ , and  $M$  points with the matrices sizes of 19, 13, and 7, respectively. While all true bound states, both below and above the vacuum edge, were found to reproduce those previously obtained numerically, in addition, complex eigenvalues, which correspond to resonances, have been found. Results of this calculation are collected in Table I.

Resonances in the excitation spectra of a quantum-mechanical system physically manifest themselves in elas-

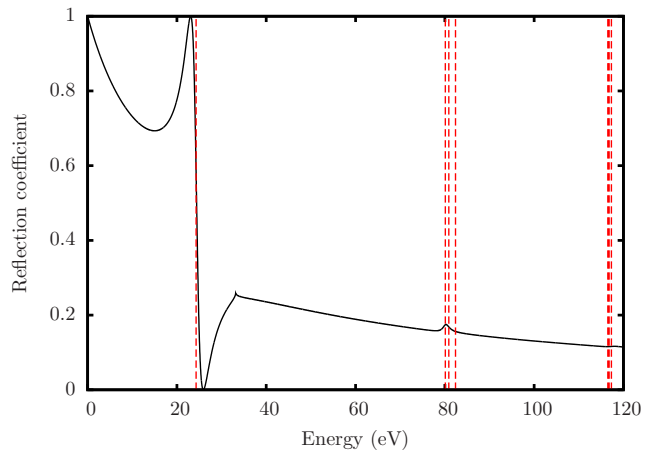


FIG. 4. (color online) Energy dependence of the coefficient of reflection of an electron from our model system. The incidence is normal to the layer ( $\mathbf{k} = \mathbf{0}$ ). The vertical dashed lines indicate the position of the resonances at  $\Gamma$  point from Table I.

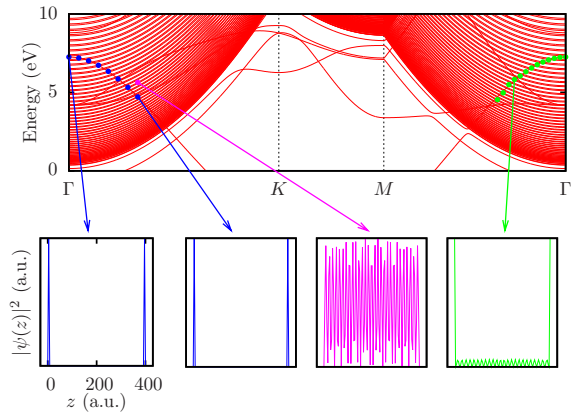


FIG. 5. (color online)  $z$ -dependence of the wave-functions of the states above the vacuum level in graphene obtained in *ab initio* repeated-geometry calculation. Plots a) and b) suggest bound states inside the continuum at  $\Gamma$  point and a point on the  $\Gamma - K$  line. In contrast, plot d) suggests a resonant character of the states on the  $\Gamma - M$  line. Plot c) exemplifies the wave-function of an arbitrary continuous spectrum state.

tic scattering at real energies in the vicinity of the complex eigenvalues [12]. In Fig. 4 we plot the coefficient of reflection of an electron incident normally onto our model system. The features in the reflectance spectrum clearly agree with the resonances' positions listed in the first column of Table I ( $\Gamma$  point). The advantage of using the reflection spectrum for studying the resonances is that this task does not require the solution of the eigenvalue problem and it is performed at real values of the energy.

From the model, we now return to the graphene problem. The only information on the character of the states

above the vacuum level that can be derived from an *ab initio* calculation within the repeated-geometry is the localization of the wave-functions around the layer. In Fig 5, we plot  $z$ -dependence of the modulus squared of the wave-functions of some representative states in  $\Gamma$  point, on the  $\Gamma - K$ , and on the  $\Gamma - M$  lines [14]. For the chosen states in  $\Gamma$  point and on the  $\Gamma - K$  line, the wave-function behavior suggests a bound state with no detectable probability of an electron to be found in the intermediate region between the layers. On the contrary, for the points on the  $\Gamma - M$  line, the probability spills out of the layer and has a nonzero distribution over the whole of the inter-layer region. This behavior suggests that the state is not a bound one although the spill-out of the electron density is small. Our previous model analysis suggests that these states become resonances having acquired final life-times. The third from the left inset in Fig. 5 shows the wave-function of an arbitrarily chosen state of (quasi-) continuous spectrum.

In conclusion, we have found that the band-structure of a stand-alone 2D-periodical quantum-mechanical system above its vacuum level is strongly affected by the possibility for a particle to escape from the corresponding state into vacuum. The overall picture of the 2D bound states' either survival or disappearance has been drawn using a simple model of a periodic potential in  $xy$  plane complemented with the  $\delta$ -function well in the perpendicular direction. Our analysis performed within this model suggests that the possibility for a particle to escape into vacuum leads to the bound states of low symmetry turning into resonances, while the bound states of higher symmetry survive up to high energies above the vacuum level.

Our model analysis has proven relevant to the *ab initio* characterization of high-lying 2D energy-bands of the stand-alone graphene confirming that the true bound-states either survival or turning into resonances is determined by the symmetry of the corresponding  $\mathbf{k}$  point.

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